OBSERVATIONS ON THE RARE EARTHS: SOME STUDIES IN THE ABSORPTION SPECTRA

BY

JOHN CALVIN BRANTLEY

A.B., Northeast Missouri State Teachers College, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The absorption spectra of the rare earth ions, both in crystals of their salts and solutions of their salts, have undergone intensive investigation in the last sixty years (5, 8). However, the question as to what energy transitions are responsible for their spectra has never been completely solved. Most workers now accept the postulation that the transitions arise in the 4f level of the atom between energy levels of differing L and S quantum numbers, but with the individual l values remaining the same. Although such transitions are forbidden by Laporte's rule, it is generally assumed that they are allowed in the rare earth ions by the presence of a potential field, a resultant of the deformation of the ion and an interaction of the 4f level with the potential field due to the neighboring negative ions (2, 3, 6).

The present study was undertaken to investigate the spectrophotometric estimation of the rare earth ions in solutions of their salts and to measure changes observed in the spectra when complexing anions were present, with the idea of possibly establishing the compositions of any complex ions by the use of the method of continuous variations (4, 7) and the method of limiting logarithms (1).

Materials And Apparatus

The rare earth materials used in this study were the most nearly pure obtainable and were taken, for the most part, from the stocks of the University of Illinois. They were of atomic weight purity or of known purity.

The spectra were measured on the Beckman Spectrophotometer, Model DU, using the standard, square, one centimeter cells which were provided by the manufacturer.

Experimental

To determine the absorption coefficients of rare earth solutions of known concentrations, weighed amounts of the oxides were dissolved in small excess of the desired acid, any excess being removed by evaporating to dryness a sufficient number of times. The residues were dissolved in distilled water in such volume as to give a concentration of rare earth metal of 25 grams per liter. These solutions were then examined with the spectrophotometer over a range from 2200 A to 10000 A. Completeness of resolution was determined by varying the slit width, that is the nominal band width of the light beam. Adherence to Beer's Law was checked by measuring the absorption coefficients of a series of volumetric dilutions of the original solution.

Studies of the effects of added anions were carried out by measuring the absorption spectra of solutions of known concentrations containing known ratios of the added anion to the rare earth ion. Only neodymium and erbium ions were studied in this way, the assumption being made that they would be representative of the cerium earth and yttrium earth series, respectively.

Results

The complete absorption spectra from 2200 A to 10000 A were determined for many of the rare earth ions in chloride, nitrate, acetate, and perchlorate solutions. Lanthanum, cerium (III), europium, gadolinium, and lutecium, as well as yttrium, scandium, and thorium exhibited no absorption in the visible or infra-red regions, but certain of these ions, namely cerium (III), europium, and gadolinium do exhibit ultraviolet absorption. Ytterbium absorbs only in the near infra-red. All other tripositive rare earth ions exhibit visible and ultraviolet absorption.

In a study of the chloride solutions of the tripositive rare earth ions, it was shown that the spectra of europium, gadolinium, and erbium were very markedly affected by

changes in the slit width and were not completely resolved at any slit width obtainable with the instrument. Samarium bands were very nearly resolved and did have a constant and reproducible absorption coefficient. The spectra of gadolinium chloride and acetate solutions were resolvable into six separate lines between 2700 A and 2800 A at a slit width of 0.060 mm. where only one diffuse band at 2730 A was obtained at a slit width of 0.329 mm.

Chloride solutions of praseodymium, neodymium, samarium, europium, thulium, and ytterbium and the perchlorate solutions of erbium obeyed Beer's Law at concentrations varying from 5 grams of metal per liter to 40 grams per liter. It was also shown that the absorption coefficients of the bands chosen for analysis of the cerium earths were unaffected by excess chloride ion, either as excess acid or as ammonium chloride. Chloride solutions of the yttrium earths were unstable with respect to the absorption intensity over a period of time and exhibited large increases in intensity with excess chloride ion present. The perchlorate solutions of the yttrium earths were stable and unaffected by excess perchlorate ion. Thus, the perchlorate solutions of the yttrium earths are to be preferred for analytical purposes.

A spectrophotometric study of the effects on the neodymium spectrum of the acetate, tartrate, and ethylenediamine tetracetate ions was carried out. Only two complex ions were indicated to be present. Using the continuous variations procedure it was found that ethylenediamine tetracetate ion forms a 1:1 and a 2:1 complex with neodymium.

Evidence was found that the neodymium ion formed a stable ionic configuration in solution with the acetate ion or tartrate ion when either of these ions was present in a ratio to neodymium of 6:1. The tartrate-neodymium arrangement was stable only in basic solution. At the 6:1 ratio of tartrate to neodymium, the 5750 A band of neodymium chloride solutions was split into three bands at 5765 A, 5805 A, and 5835 A. This was the only band which was split, but all the others were shifted to the red.

The ethylenediamine tetracetate ion in basic solution, when mixed in varying proportions with neodymium chloride solutions, caused a splitting of all the strong sharp bands of the neodymium ion on the red side of 5100 A. The splitting was found to increase as the concentration of ethylenediamine tetracetate ion was increased. The 5750 A band was split into six well-defined bands between 5750 A and 5860 A for the largest concentration of this ion. The ionic configuration of this ion with the neodymium ion is apparently very stable, but no ratio was found which gave a maximum effect on the spectrum.

The chloride ion apparently forms stable configurations with the erbium ion in perchlorate solutions when the ratio of chloride to erbium is 3:1 or 6:1. The bands of erbium perchlorate were found to be split when the ethylenediamine tetracetate ion was added. All strong sharp bands were split into at least two bands.

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VITA

The author was born on August 20, 1921, in Newtown, Missouri. He attended the public schools in Centerville, Iowa, and Unionville, Missouri, graduating from the Unionville High School in 1939. That year, he entered the Northeast Missouri State Teachers College in Kirksville, Missouri, receiving the Bachelor of Arts degree from this institution in 1942. He was then employed as Scientific Aide at the Northern Regional Research Laboratory, USDA, Peoria, Illinois, until June, 1943, when he entered military service. Upon discharge from the Army Chemical Warfare Service in November, 1945, he was reemployed as Chemist, P-1, at the Northern Regional Research Laboratory. He left this position in August, 1946, to enter the Graduate School of the University of Illinois. From February, 1947, to September, 1947, he was employed as Research Assistant by the Department of Chemistry, University of Illinois. From September, 1947, to June, 1949, he held the position of Research Assistant on the University of Illinois Rare Earth Research Program sponsored by the Office of Naval Research.

The author is a member of the American Chemical Society, Sigma Xi, and Phi Lambda Upsilon.

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